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LASER INDUCED REACTION FOR PRE-BOND
SURFACE TREATMENTS OF
ALUMINUM ALLOYS

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Annual Report 3.91 - 3.92

Financed by the US Air Force (AFOSR)

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CHESTER J. DYMEK, Lt Col, USAF
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SEM observation of the laser treated Al alloy surface (before adhesion) did not show any morphological changes at laser energy of 0.2 J/P/cm^2 . However, at laser energy of 0.7 J/P/cm^2 , some morphological changes were detected. SEM analysis of joint failure surfaces exhibited changes of the locus of failure from adhesive to cohesive type as the number of the laser pulses increases.

The enhanced mechanical properties were supported by visual inspections and SEM micrographs indicating a change of failure mode from adhesive (nontreated) to mostly cohesive (laser treated).

Durability studies of the laser pretreated joints in hot-humid environments proved that the laser treatment is durable to hydro-thermal environment when primed before adhesion close to the durability attained with chromic anodization.

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1. INTRODUCTION

Proper surface treatment of adherends is among the decisive factors with respect to the final quality and durability of an adhesive joint.

Many treatments have been devised for preparing metal surfaces for adhesive bonding, painting and the like. The general purpose of these preparation procedures is to modify the original surface of the metal (a) to promote development of interfacial bonds to adhesives and (b) to enhance the environmental resistance to moisture and humidity effects.

The pretreatments which are commonly used for aluminum as corrosion resistant coatings or adhesion promoters are: chromate conversion coating, chromic acid anodization (with or without sealing), sulfuric acid anodization (with or without sealing), phosphoric acid anodization (PAA) and chromic sulfuric etch (PPL).

All these treatments involve the use of acids (sulphuric, nitric, hydrochloric), strong bases or hexavalent chromium compounds (1). New OSHA and EPA regulations ban such chemicals in industrial operations. UV lasers may offer a chemical free surface treatment for aluminum adhesion. Furthermore, the use of laser treatment offers a precise, clean and simple pretreatment method.

The potential of UV laser for prebonding treatment of thermoplastic adherends has been demonstrated in previous investigations (2,3). The treatment mechanisms involves morphological and chemical changes of the adherends' surfaces, due to conformity of UV laser energy to surface topography modification and to organic bond activation (4). It has been shown that surface treatment of Aluminum by excimer laser results in roughening and oxidation of the surface (5-7), increase of microhardness (8) and induction of surface melting (9).

Rigorous characterization of the effect of the various chemical and electrochemical preadhesion treatments on aluminum indicated morphology and chemical composition changes of the surface (10). Thus laser and

chemical pretreatments can be compared.

In the present investigation the application of excimer UV laser for surface treatment of Al alloys adherends has been studied. The objective of the work is two-fold: first, to establish the effect of excimer UV laser on the Al alloy surface microstructure using various spectroscopic methods, second, to correlate the microstructure with the macro behavior as reflected in shear loading and failure locus of adhesively bonded joints using two-part rubber modified epoxy adhesive developed previously in Rafael for field repair (11-13).

2. EXPERIMENTAL

2.1 Laser Treatment

The laser used during the course of this investigation was a UV excimer ArF Laser EMG 201 MSC production of "Lambda Physik", W. Germany (193 nm) producing a $2 \times 0.5 \text{ cm}^2$ area beam with pulse energy of 160-200 mJ/P·cm² or a concentrated beam (0.3 cm²) with higher pulse energy (730 mJ/P·cm²). Repetition rate was 30 Hz and the number of pulses ranged between 1-5000.

The specimens were moved under the beam by means of a controlled X-Y table. All experiments were conducted at ambient temperature and air environments.

2.2 Adherend and Adhesive

The substrates used throughout this work was Al 2024 T3 of nominal composition, Cu 4.4%, Mg 1.5%, Mn 0.6% and the balance Al. The substrate was wiped with Acetone prior to laser treatment.

The adherends were laser treated and bonded by a rubber modified epoxy adhesive (11-13). The adhesive is a mixture of two polyfunctional epoxy resins (ERL-510 and MY 721 product of Ciba-Geigy) cured with TETA and modified with ATBN-1300 × 16 rubber product of B.F. Goodrich (Table I). Curing was carried out at ambient temperature for 48 hours.

In some cases an epoxy terminated primer (2% A-187 in 80/20 V/V ethanol-water) was applied by brushing. The primer was allowed to dry for 1/2 hr. at R.T. and 1 hr. at 100°C. The A-187 is a product of Union Carbide.

Table I

Chemical formula

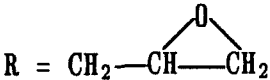
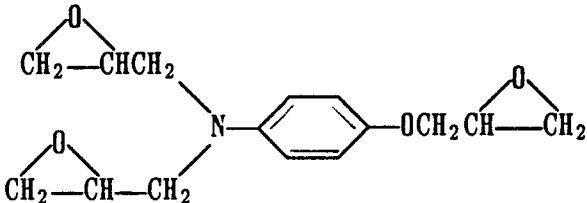
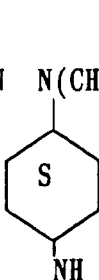
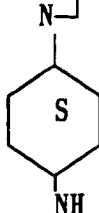
Materials	Chemical Formula	Trademark
Epoxy Resin EE=128 gr/eq	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{N} - \text{C}_6\text{H}_4 - \text{CH}_2 - \text{C}_6\text{H}_4 - \text{N} \\ \diagup \\ \text{R} \end{array}$ $\text{R} = \text{CH}_2 - \text{CH} - \text{CH}_2$ 	MY720 CIBA GEIGY
Epoxy Resin		ERL510 CIBA GEIGY
Curing Agent AEb- 40±3gr/eq	$2\text{HN}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$	TETA Miller Stephenson Chem. Co.
Rubber ATBN AE-1160 gr/eq	$\begin{array}{c} \text{O} \\ \parallel \\ \text{N}(\text{CH}_2)_2 - \text{C} - (\text{CH}_2\text{CH}=\text{CHCH})_x - (\text{CH}_2 - \underset{\text{CN}}{\text{CH}})_y - \text{C} - \text{N}(\text{CH}_2)_2 \\ \parallel \\ \text{H} \end{array}$  	Hyear ATBN 1300×16 BF GOODRICH Chem. Co.
A187 primer	$\text{CH}_2 - \text{CH} - (\text{CH}_2)_3 - \text{SiO}(\text{CH}_3)_3$	UNION CARBIDE

Table 1

2.3 Testing

The surface of the laser treated aluminum with and without primer was examined and compared to untreated adherends by FTIR (Fourier Transform IR) spectrophotometer (Nicolet 5DX) in an external specular mode, and AUGER electron spectroscopy (AES) (Physical Electronic Ind. Inc. model 590A).

Surface morphology was studied by Scanning Electron Microscopy (Jeol model JMS 840 Japan) equipped with Energy Dispersive System (EDS product of Link, model 290).

Adhesive joint properties with and without primer were determined using Single-Lap-Shear Joints (SLS) according to ASTM D-1002-72. Ten days curing elapsed before loading the shear specimens in an Instron Model 1185 at a rate of 2 mm/min at 25°C. The mode of failure was determined to be either adhesive (interfacial - 100% coverage of adherends), or cohesive (200% coverage of adherends). Fracture surfaces morphology was studied by SEM.

Durability tests were produced by a wedge test according to ASTM D-3762. The test was performed on specimens with and without primer exposed to hygrothermal conditions (60°C and 95% RH) in a humidity chamber for various durations (1, 4, 24 and 168 hours). The development of the initial crack length was measured as a function of exposure time. At the end of the test the wedge was forced open totally and the mode of failure was determined.

2.4 Methodology

Two kinds of references were used in all experiments for comparison with laser treated specimens: a non-treated bar Al set (with or without primer) and an unsealed chromic acid anodized (according to MIL-A-8625C) Al set of adherends (with or without primer). The second reference is the common preadhesion surface treatment for Al alloys (14). The level of adhesion was determined relative to the SLS strength of the anodized

and the non-treated specimens for each laser condition studied.

Three kinds of experiments were produced: laser surface treatment of bare Al alloy, laser surface treatment of A-187 primed Al alloy and laser surface treatment of bare Al alloy followed by priming with A-187. For each experiment the optimal laser conditions (energy, no. of pulses and repetition rate) were determined.

Surface chemical and morphological analysis were performed prior to and following laser treatment of the aluminum adherends and on the fractured surfaces of the SLS specimens.

The optimal laser treatment for the Al adherend with or without primer was examined for durability in a wedge test compared to chromic anodized and non-treated specimens. In an additional phase of the study the laser treatment effect on chromic acid anodized Al specimens was investigated and compared with laser effects on bare and treated Al alloys.

3. RESULTS AND DISCUSSION

3.1 Shear Strength and Failure Mode

Table II and Figure 1 give the lap shear strengths of the modified epoxy adhesive without primer for UV laser treated and untreated Al 2024 joints at various number of laser pulses and laser energy densities. It is evident that UV laser treatment has been effective on the Al adherend. The higher the number of laser pulses the greater is the adhesive bond strength.

At higher laser energy, the lap shear strength is increased by 40% compared to the unsealed chromic anodization treatment and an improvement of 600-700% compared to nontreated Al is achieved.

Increasing the energy density of the laser treatment (from 0.16 to 0.185) results in better adhesion strength until an optimum value is reached. More energetic laser treatment (0.73 J/P·cm²) reduces adhesion

strength probably due to melting effect (2).

Table 3 and Figure 2 represent the lap shear adhesion strength of the modified epoxy adhesive applied on UV laser treated and untreated Al-2024T3 joints with silane primer (A187) applied before the adhesion (after laser treatment).

Laser treatment caused an increase of the lap shear adhesion strength (figure 2). The highest value (12.8 MPa) was achieved for specimens irradiated with 600 pulses at $0.185 \text{ J/P}\cdot\text{cm}^2$. This value is lower compared to 14.3 MPa which was the highest value achieved by applying adhesive without primer after optimal laser irradiation with 2000 pulses at the same energy level (table 2, figure 1) probably due to vanishing of the morphology effect produced by the laser treatment.

The lap shear adhesion strength of the modified epoxy adhesive applied on laser treated primed Al joints are given in table 4 and figure 3. The results show that laser treatment of the primer caused a slight increase of the shear adhesion strength to a maximal value of 7.25 MPa which was reached by irradiation with 60 pulses. Further increase of pulse number caused a sharp decrease of the lap shear strength to about 5 MPa at 200 pulses and remained at this level up to 2000 pulses (Figure 3) probably due to primer ablation.

Visual inspection of the failure surfaces shows clearly that laser treatment causes a dramatic change in the mode of failure from adhesive (interfacial) in non-laser treated adherend to mostly cohesive at optimal laser energy condition treatments indicating that the interfacial adhesion was significantly improved.

Visual inspection revealed the same phenomena when primer was applied on the irradiated area before adhesion.

The mode of failure of the joints with irradiated primer was mostly adhesive due to primer ablation by laser irradiation, thus the interfacial adhesion was not improved.

Table II

The effect of laser pretreatment of Aluminum (2024 - T3) on
lap shear adhesion strength

SAMPLE	LASER ENERGY J/P·cm ²	REPETITION RATE HZ	No. of PULSES	SHEAR STRENGTH MPa **	FAILURE TYPE c/a/m *
Untreated Al (ref.)	-	-	-	2.03 ± 0.20	a
Anodized Al (ref.)	-	-	-	10.20 ± 0.80	a
Laser Treated Al	0.16	Manual	10	4.17 ± 0.45	m
	0.16	30	1000	7.95 ± 0.20	m
Laser treated Al	0.73	Manual	10	5.11 ± 0.32	m
	0.73	30	200	5.30 ± 0.5	m
	0.73	30	600	4.16 ± 0.4	c
	0.73	30	1000	5.40 ± 0.5	c
Laser treated Al	0.185	Manual	1	2.45 ± 0.47	a
	0.185	30	200	12.33 ± 0.5	c
	0.185	30	600	11.59 ± 0.45	c
	0.185	30	1000	11.63 ± 0.57	c
	0.185	30	2000	14.39 ± 0.20	m/c
	0.185	30	5000	14.25 ± 0.30	m/c

* c = cohesive, a = adhesive, m = mixed failure

** five specimens were used for each test.

Table III

The effect of laser pretreatment of aluminum (2024-T3) on
lap shear adhesion strength (adhesive with primer)

SAMPLE	LASER ENERGY J/P cm ²	REPETITION RATE HZ	No. of PULSES	SHEAR STRENGTH MPa **	FAILURE TYPE c/a/m *
Untreated Al (ref.)	-	-	-	2.03 ± 0.4	a
	0.195	Manual	1	6.55	m/a
	0.195	30	200	7.16 ± 0.15	m/a
	0.195	30	600	12.8 ± 0.7	c
	0.195	30	1000	11.7 ± 0.18	c
	0.195	30	2000	12.4	c
	0.195	30	5000	12.69	c

Table IV

The effect of primer treatment on lap shear
adhesion strength of aluminum

SAMPLE	LASER ENERGY J/P cm ²	REPETITION RATE HZ	No. of PULSES	SHEAR STRENGTH MPa **	FAILURE TYPE c/a/m *
Untreated Al (ref.)	-	-	-	3.43	a
	0.185	Manual	1	4.65	a
	0.185	5	20	6.53 ± 1.95	a
	0.185	10	60	7.24 ± 0.88	a
	0.185	10	100	5.86 ± 0.22	a
	0.185	10	200	4.52	a
	0.185	10	500	5.07 ± 0.16	a
	0.185	10	1000	4.76 ± 0.65	a
	0.185	10	2000	5.22	a

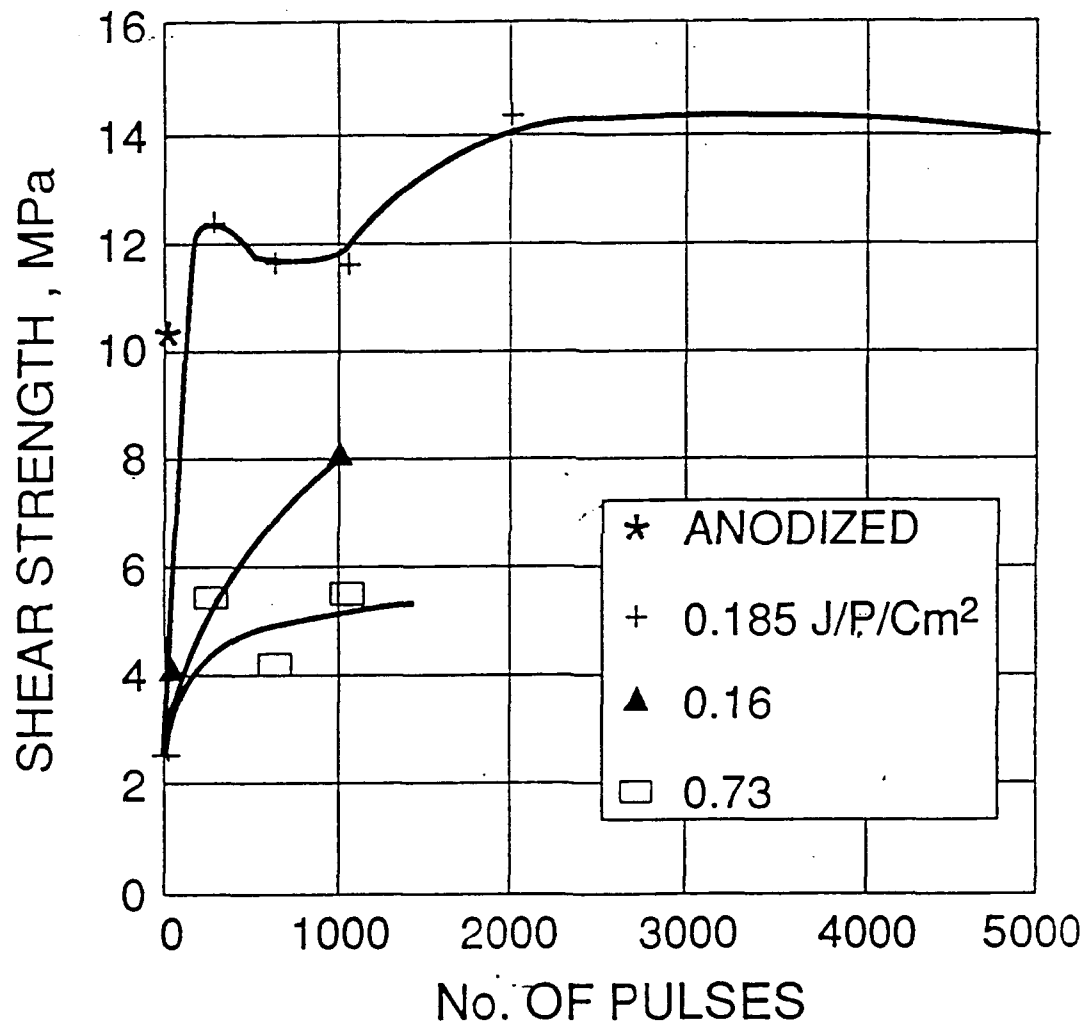


Fig. 1: Lap shear adhesion strength of laser treated Al as function of laser pulses (adhesive without primer).

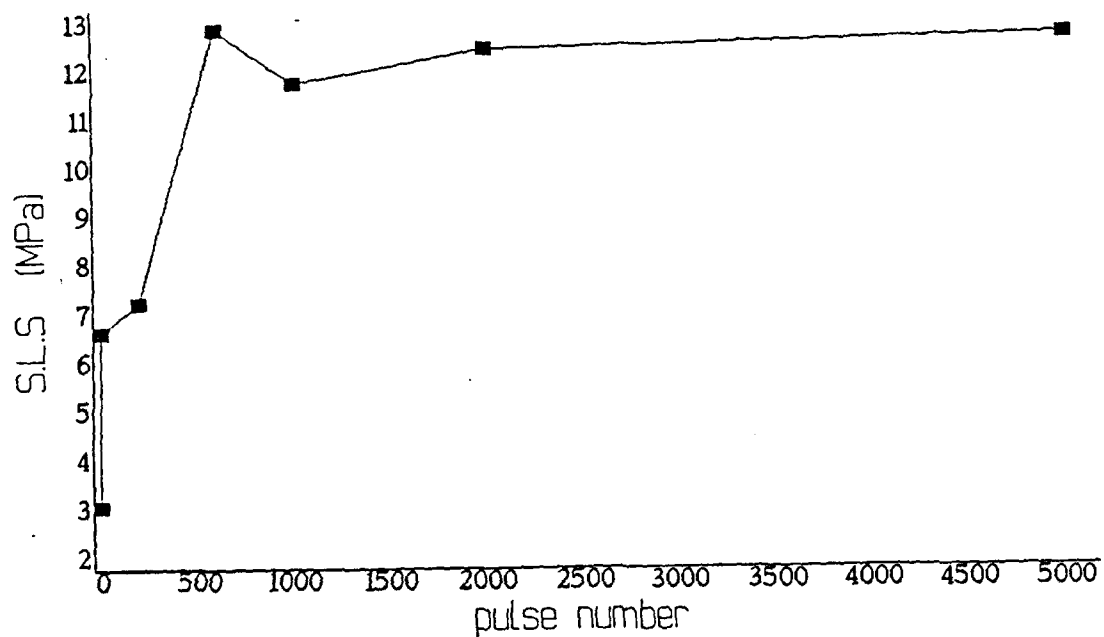


Fig. 2: Lap shear adhesion strength of laser treated Al as a function of laser pulses (adhesive with primer)

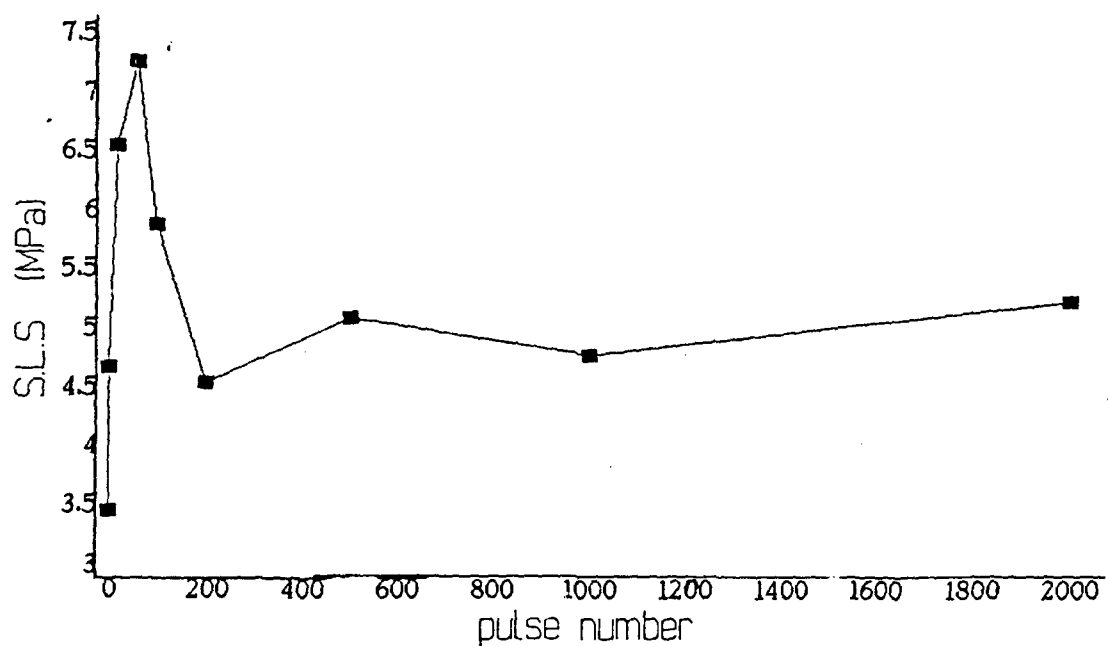


Fig. 3: Lap shear adhesion strength of joints with laser treated primer as a function of laser pulses (adhesive with primer)

The effect of laser treatment on adhesion strength of unsealed chromic anodized Al 2024 is presented in Table V.

It can be seen that UV laser treatment of the unsealed chromic anodized aluminum adherend reduces the shear strength of the joint at all the laser conditions tested, probably due to destruction of the fine anodized layer microstructure by the laser irradiation. Thus, no further study was pursued in this direction.

3.2 SEM

SEM micrographs of the Al adherent after laser treatment showed no morphological changes at low laser energies (Fig. 4a). Increasing the laser energy reveals a fine microstructure of the treated surface demonstrating array of cracks about 1μ wide and small holes (Fig. 4b). Increasing the number of pulses results in a finer surface microstructure of the crack nets, larger holes and exposed inclusions. The edges of the holes and cracks are smooth (Fig. 4c).

Figs. 5-7 represent the fractured adhesive surfaces of SLS joints with Al adherents treated with various laser conditions. Figs. 8-10 show the fractured adhesive surfaces of SLS joints with laser treated Al adherents primed with A-187.

The morphology of the fractured surfaces seemed similar for both types of treatment.

SEM micrographs of the fractured adhesive surfaces exhibit a smooth adhesive interfacial failure in non laser treated adherends and at 1 pulse laser treatment (Figs. 5 a,b and Fig. 8. Raising the number of pulses to 200 results in a rough cohesive failure typified by the modified epoxy microstructure (filled with rubber particles) (11,13) (Fig. 6a,c, Fig. 9a,b).

Table V

The effect of laser pretreatment of unsealed chromic acid
anodized aluminum on lap shear strength

Anodized Al		
No. of Pulses*	Shear Strength	Failure Type
(ref.) 0	10.2 ± 0.8	c
100	7.2 ± 0.6	a
1000	8.39 ± 0.7	c

* Laser energy $0.185 \text{ J/P} \cdot \text{cm}^2$

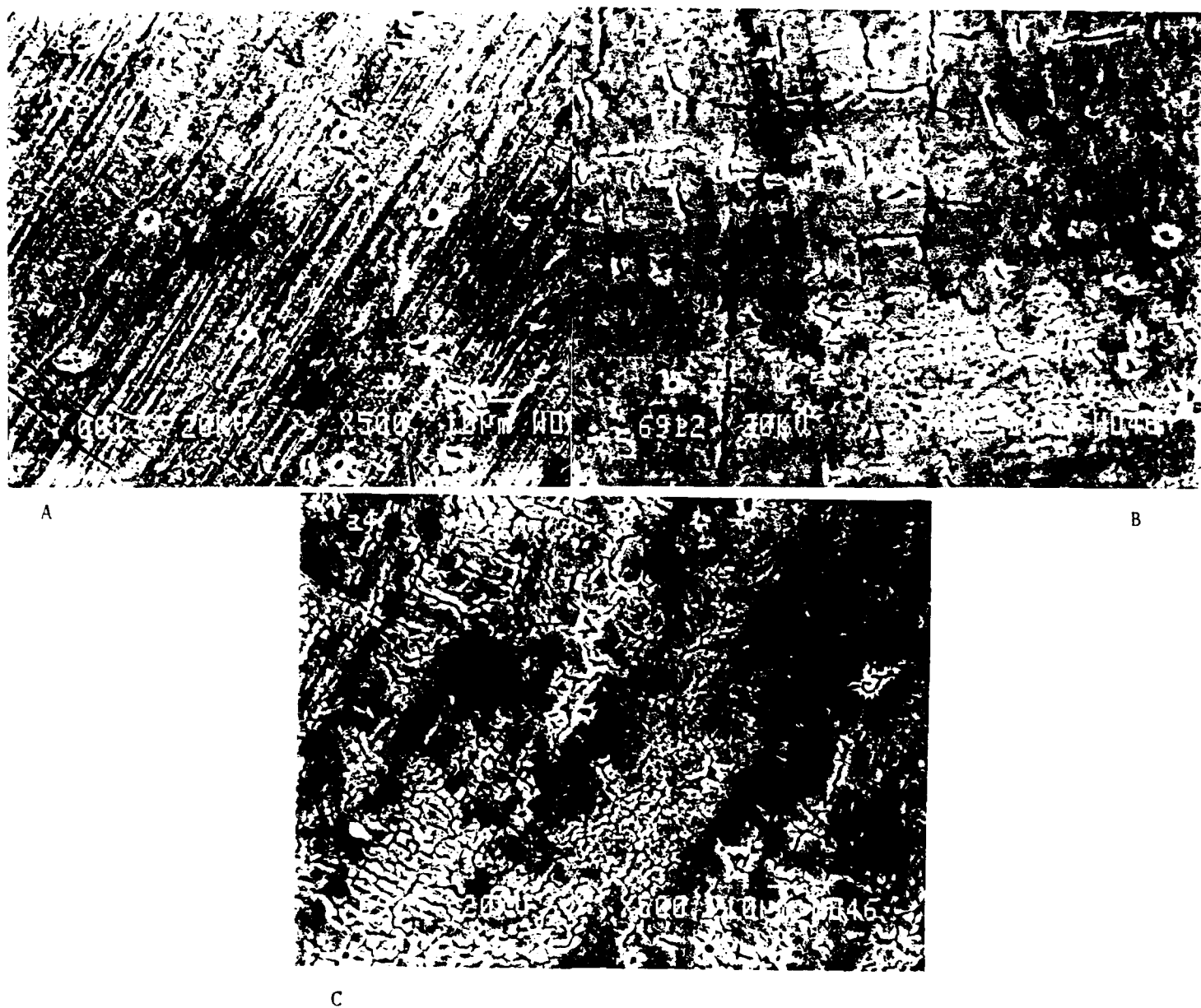


Fig. 4: SEM micrographs of laser irradiated Al specimens ($\times 500$)
(a) untreated (b) 200 P (c) 2000 P ($0.73 \text{ J/P} \cdot \text{cm}^2$).

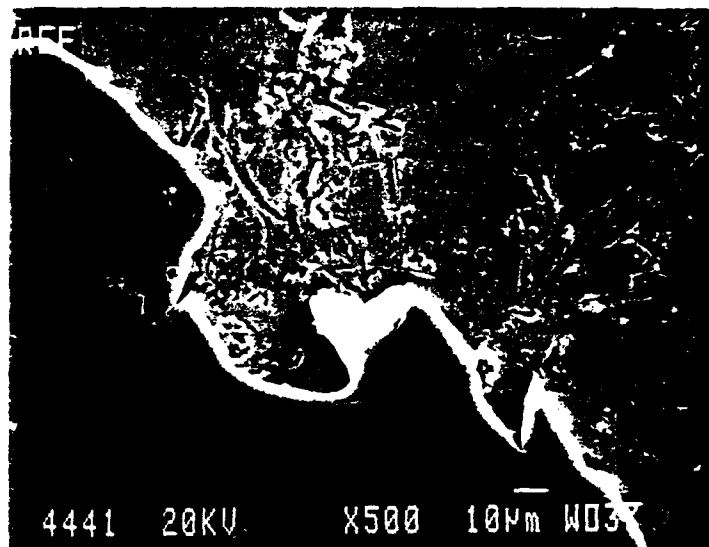
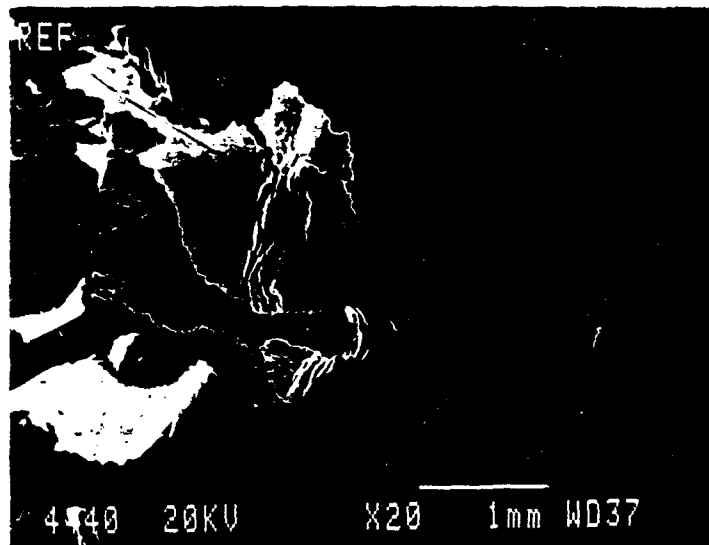
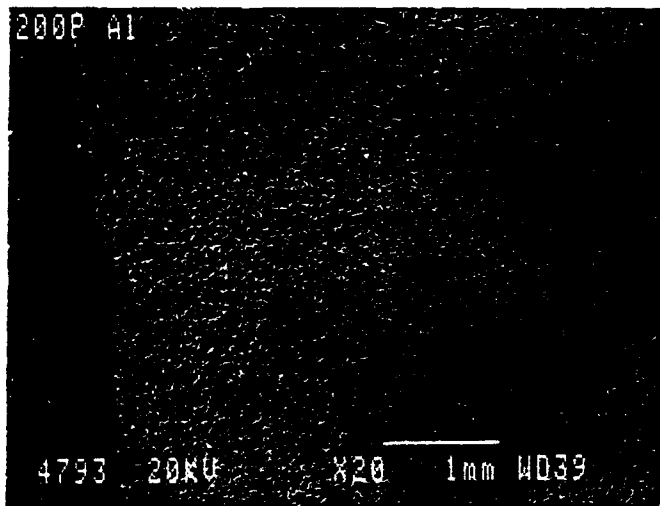
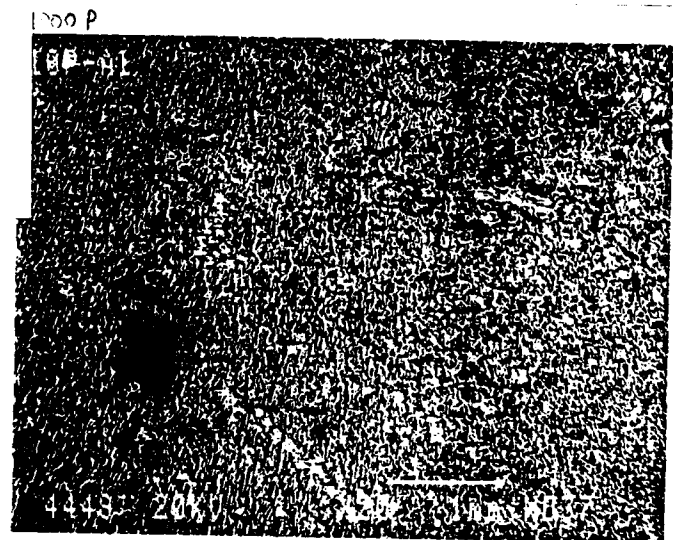


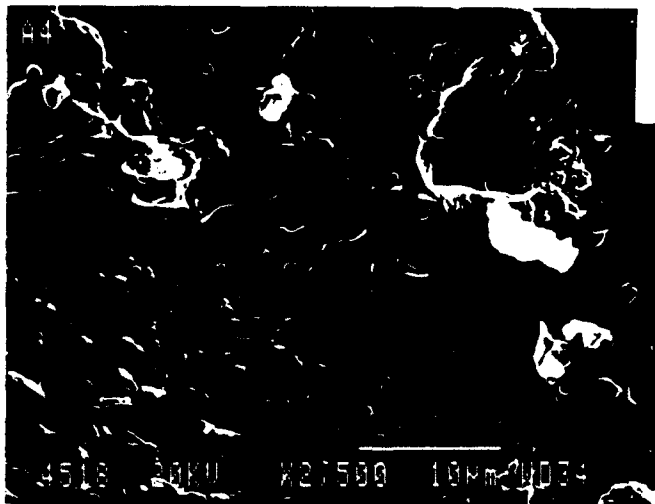
Fig. 5: SEM micrographs of failure surfaces of untreated Al ($\times 20, 500$).



A



B



C

Fig. 6: SEM micrographs of failure surfaces of laser treated Al specimens (a) 200 P $0.25 \text{ J/P}\cdot\text{cm}^2$ ($\times 20$) (b) 1000 P, $0.16 \text{ J/P}\cdot\text{cm}^2$ (c) typical cohesive microstructure ($\times 2500$).

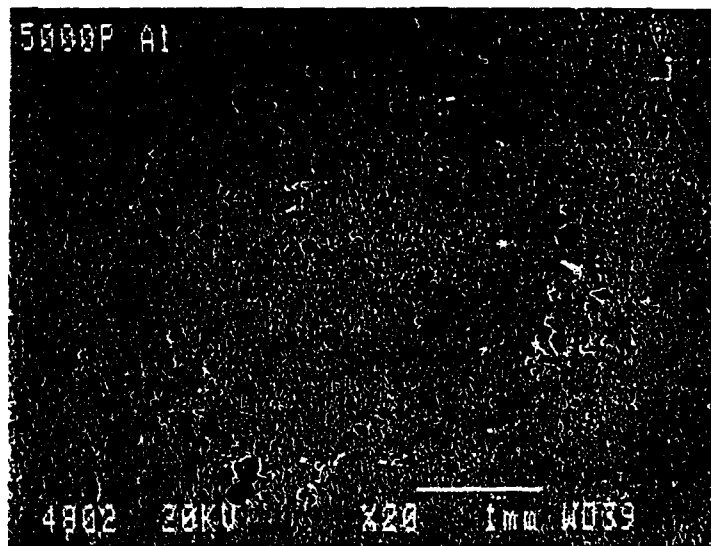
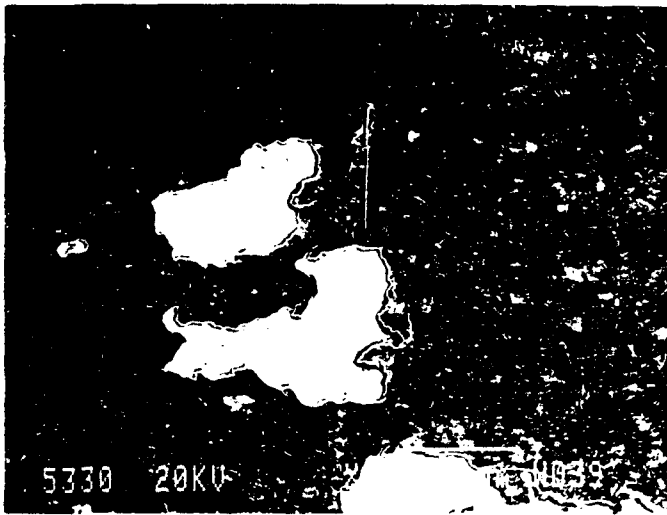


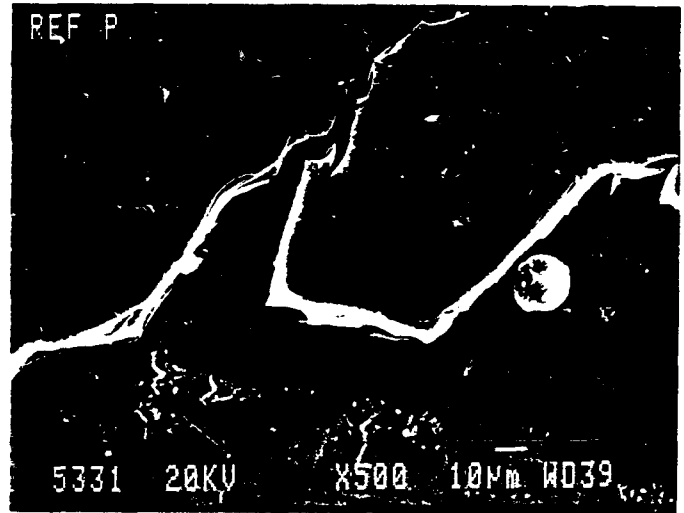
Fig. 7: SEM micrographs of failure surface of laser treated Al specimen (5000 P, 0.2 J/P·cm²).

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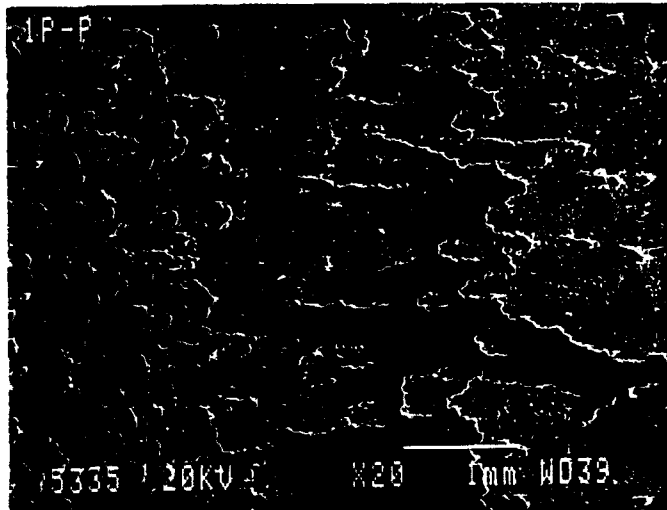
A

REF P



B

1P-P



C

1P-P

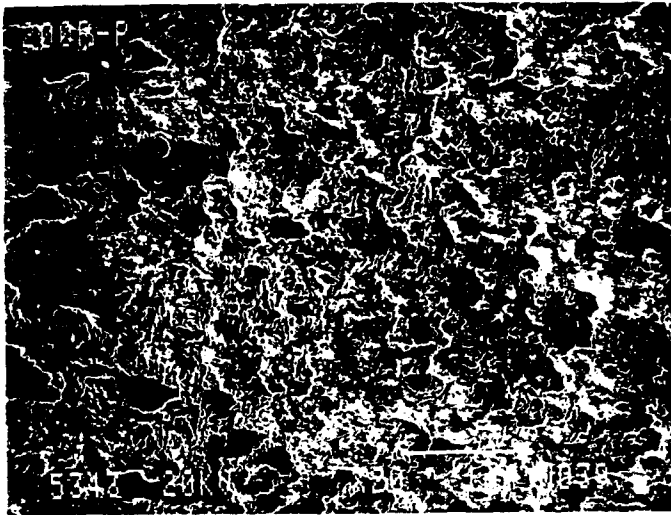


D

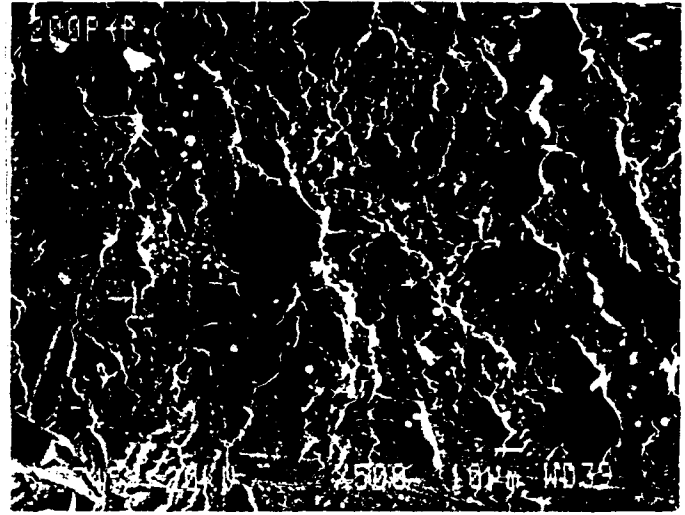
Fig. 8: SEM micrographs of failure surfaces. Rubber modified epoxy with primer.

A,B: Untreated Al, ($\times 20$, $\times 500$).

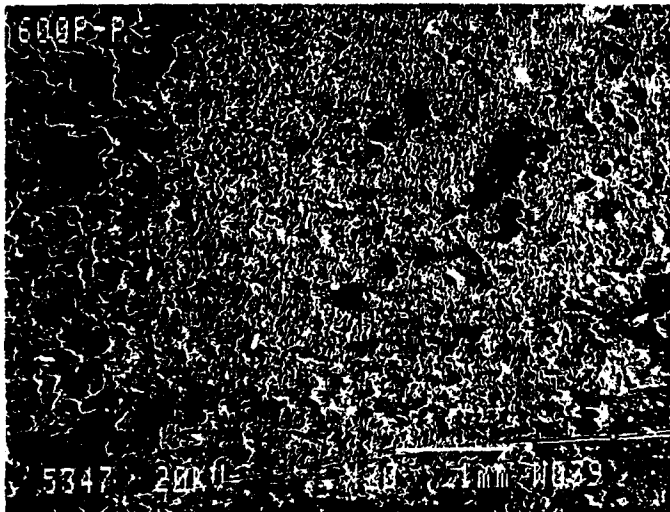
C,D: Laser treated with one pulse at laser energy of $0.185 \text{ J/P}\cdot\text{cm}^2$, ($\times 20$, $\times 500$).



A



B

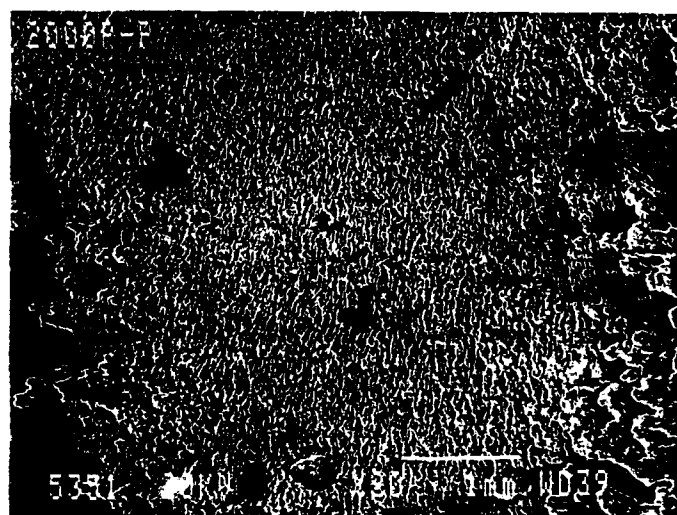


C

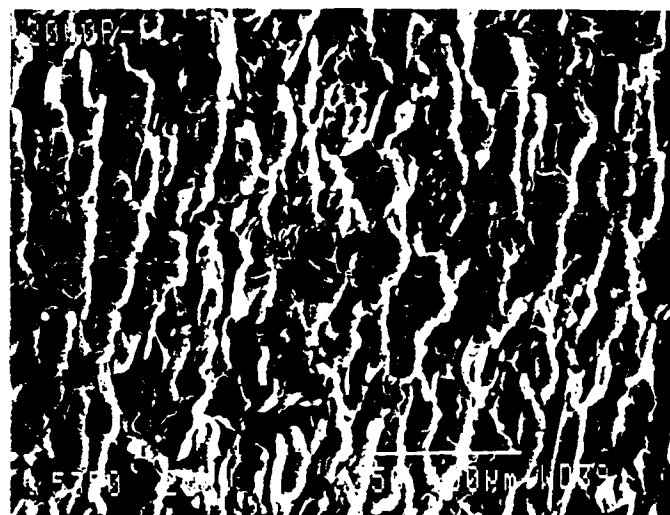


D

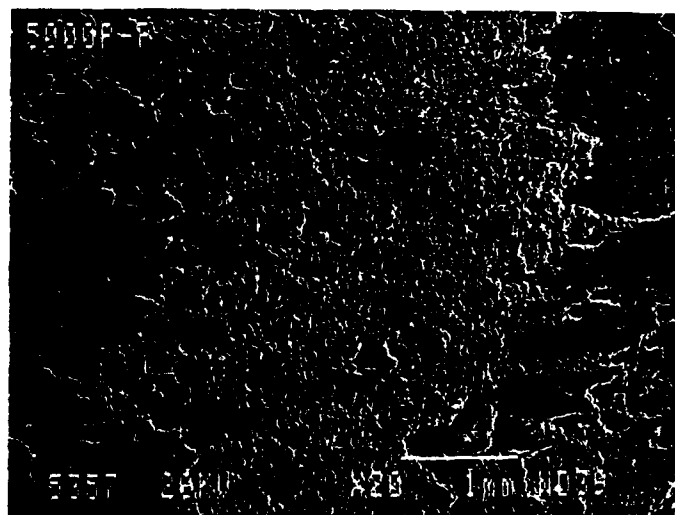
Fig. 9: SEM micrographs of cohesive failure surfaces, after laser treatment. Rubber modified epoxy with primer.
 A,B: 200 pulses, $0.185 \text{ J/P} \cdot \text{cm}^2$ ($\times 20$, $\times 500$)
 C,D: 600 pulses, $0.195 \text{ J/P} \cdot \text{cm}^2$ ($\times 20$, $\times 250$)



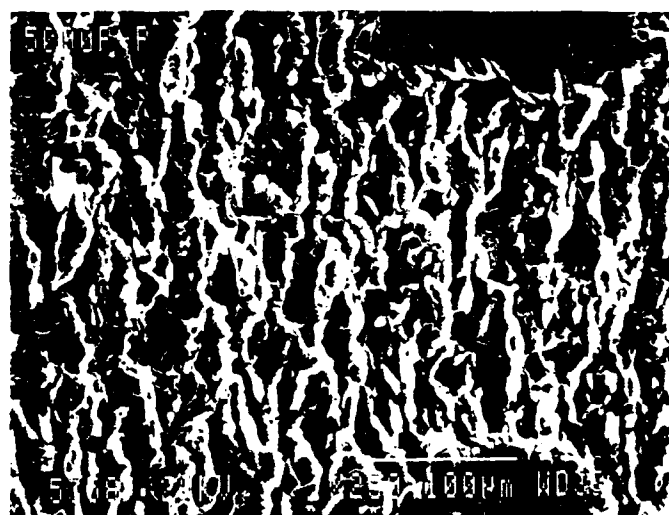
A



B



C



D

Fig. 10: SEM micrographs of cohesive failure surfaces, after laser treatment. Rubber modified epoxy with primer.

A,B: 2000 pulses, $0.185 \text{ J/P} \cdot \text{cm}^2$ ($\times 20$, $\times 250$)

C,D: 5000 pulses, $0.195 \text{ J/P} \cdot \text{cm}^2$ ($\times 20$, $\times 250$)

At higher number of pulses, i.e., 1000-2000 pulses ($0.185 \text{ J/P}\cdot\text{cm}^2$) the micro fractograph reveals a finer cohesive structure having the same microstructure (Fig. 6b, Fig. 9c,d, Fig. 10a,b). At 5000 pulses a mixed failure (but still mostly cohesive) is observed (Fig. 9, Fig. 10c,d) probably due to surface damage (Fig. 4). Damage of the adherend's surface results in regional melting exposing smooth rounded areas which are less suitable for adhesion. It also creates weak surface layers which can be easily peeled off by external forces (2).

3.3 FTIR

In addition to morphological modifications at high laser energies, chemical changes were detected by FTIR. The main FTIR absorptions for the various laser treatments on Al 2024 are shown in Fig. 11. Untreated Al shows no absorptions of any oxide layer. The higher the number of laser pulses applied to the Al surface the stronger are the absorptions of the oxide layer (Fig. 11). On the other hand, gradual increase of the laser energy results in different chemical effects on the Al surface. The absorption peaks at 3600-3700 are stronger at higher laser energy, probably due to water accumulation at the surface. The absorption peak at 950 cm^{-1} (Al-OH) disappears, and a new peak at 1630 cm^{-1} (Al-O+H₂O), develops at high laser energies. These effects are similar to those shown in chromic acid anodization (9,11). At lower laser energies the IR spectrum of the oxide layer is similar to that of the unsealed chromic acid oxide layer and at higher laser energies to the sealed one (13).

FTIR absorptions of the various laser treatment on primed Al 2024 are compared and summarized in Table VI. It can be clearly seen that absorptions typical to the primer such as Si-O-Si (1144 cm^{-1}), Si-CH₃ (1419) decrease gradually revealing ablation. Absorption at 1716 cm^{-1} (C=O) and Al-O-Al and Al=O increase due to oxidation. Absorption at 1341 (Si-O-Al) indicate an organo-metallic bond of the primer with the adherent. The growth of the oxide layer is suppressed due to the washing of the primer.

3.4 Auger

Auger surface and depth profiles of laser treated and untreated Al specimens shed more light on the effect of the laser treatment. It can be seen that on the surface of untreated Al, mainly C, Al and O are present and small amounts of Cu and Mg and other contaminants (Fig. 12a). At lower laser energies the surface is cleaned from both natural oxides grown on the bare Al alloys and other contaminations such as Carbon compounds (Fig. 12b). At high number of pulses probably a new oxide layer grows (Fig. 12c).

Comparing the depth profile of laser treated and untreated Al (Fig. 13) reveals that the main effect of the laser treatment at low number of pulses is the removal of the carbon compounds present in the untreated oxide. Carbon content in the surface of the untreated Al is as high as 55% Atomic Concentration (A.C.) (Fig. 13a) and decreases gradually to 10% A.C. at the depth of 3000 Å (Fig. 13b,c). For the laser treated Al carbon content at the surface is only 15% A.C. (Fig. 13d) decreasing to 5% A.C. at the depth of 15 Å (Fig. 13e). At higher number of pulses an oxide layer reappears (Fig. 13e,f). The oxide layer of the untreated Al is 950 Å deep while the new oxide layer grown on the treated Al is only 550 Å thick. The oxidized layer of the laser treated and untreated Al consists of both Al and Mg oxides. Comparing the relative amounts of O:Al reveals that the oxides grown on the laser treated Al are richer with oxygen compared to the untreated ones (O:Al = 4.5:2 for untreated Al, O:Al = 5:2 for 200 p. and O:Al = 6.7:2 at 2000 p. treatment). No similar effects were found in the chromic acid anodization treatment (13).

3.5 Durability

The results of the durability wedge test with and without primer at the optimal laser condition r.r = 30 Hz, energy = 0.185 J/P·cm² and 2000 p are summarized in Fig. 14.

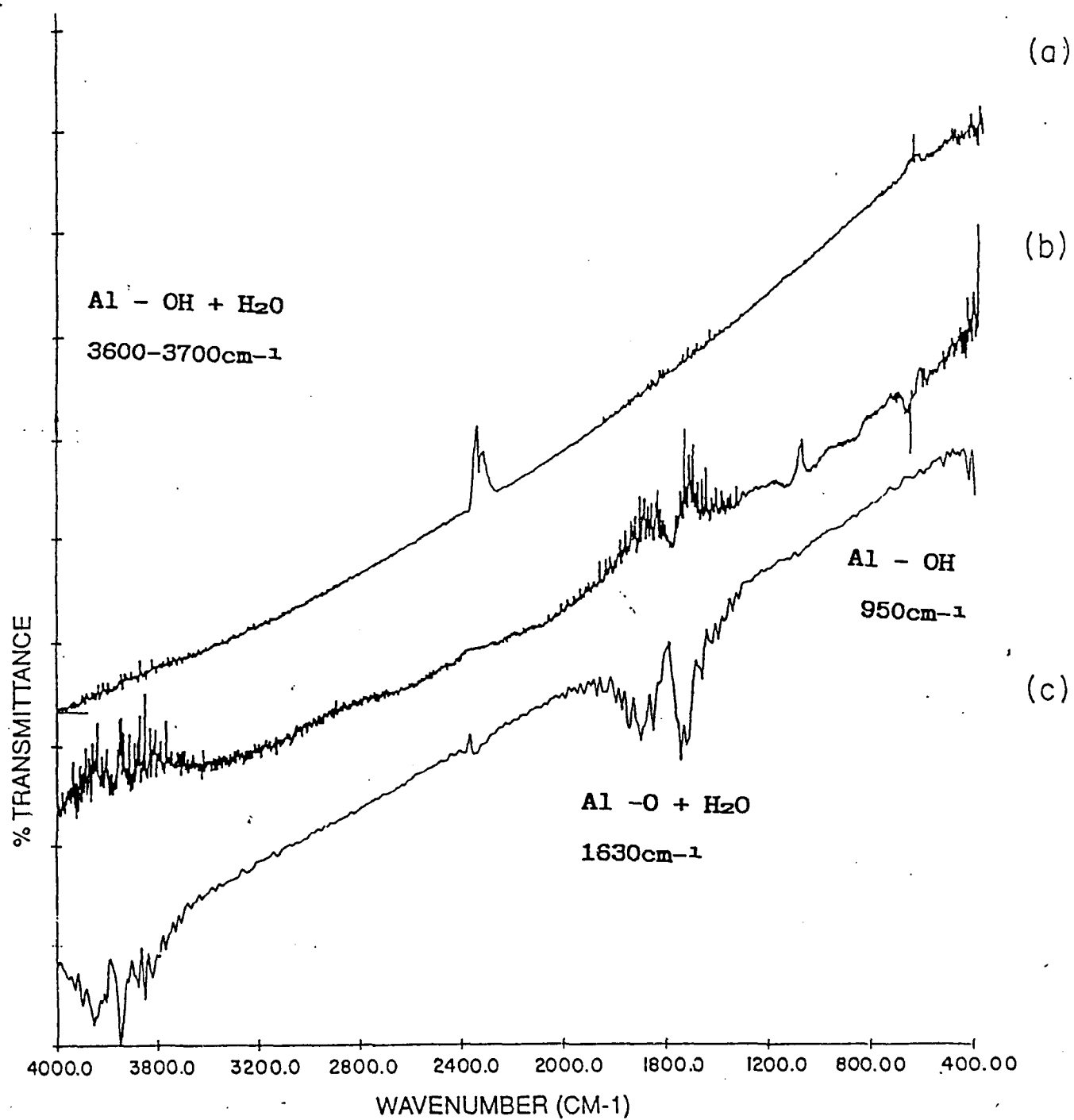
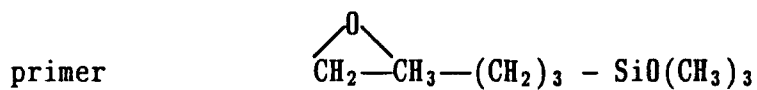


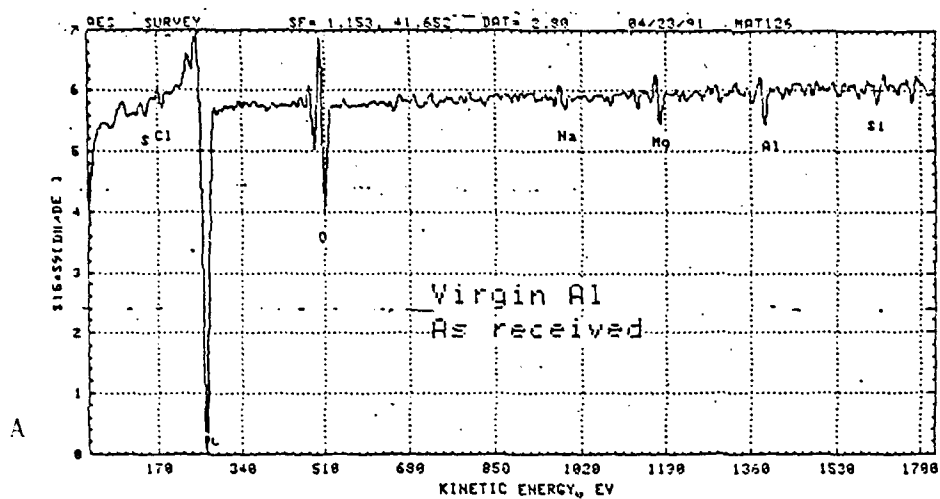
Figure 11: FTIR Spectra of Untreated and Laser Treated Al.

- (a) Untreated Al (b) Laser treated 0.185 J/P·cm² 200 pulses
(c) Laser treated 0.73 J/P·cm² 200 pulses.

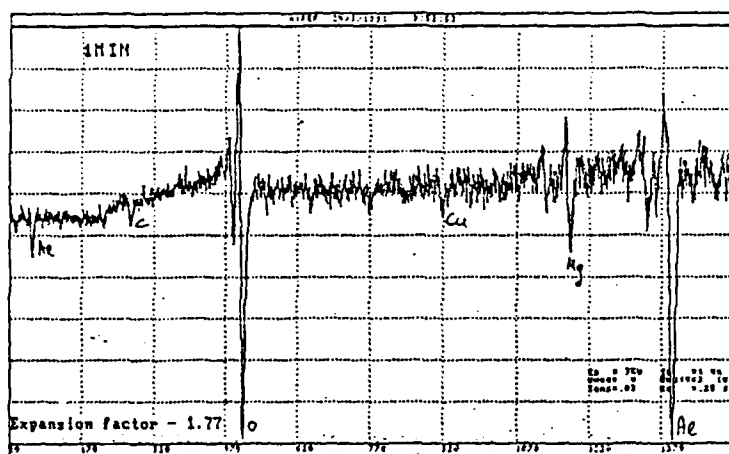
Table VI
FTIR Absorption

Absorption		Ref.	I r r a d i a t i o n C o n d i t i o n s						
			1P	20P	60P	100P	200P	500P	1000P
3648	H ₂ O	0.8	-	2.6	3.6	3.5	4.1	3.8	4.2
3736		1.7	-	2.5	3.0	3.0	3.8	3.5	3.3
1716	C=O	0.8	1.4	1.8	2.5	3.2	3.3	2.9	2.8
1541	C=C-C	0.8	1.9	2.4	3.4	4.5	4.7	3.9	3.9
1144	Si-O-Si	1.1	1.0	1.0	-	1.0	0.7	0.6	0.4
1097	Al-O-Al	1.3	1.1	1.1	-	1.6	1.5	1.0	0.9
1419	Si-CH ₃	-	0.6	0.7	0.9	1.2	1.3	1.2	1.1
1456	Al-O	-	1.0	1.3	1.8	2.3	2.5	2.1	2.2
1341	Al-O-Si?	-	-	0.5	0.8	1.1	1.1	1.0	1.0
860	Al-O-Al	0.6	0.5	0.5	-	0.7	0.6	0.6	0.5
667	?	1.1	0.8	0.8	0	0	0	0	0
610	?	1.2	1.0	1.0	-	1.2	1.3	1.0	0.8
634	?	-	-	0.7	1.5	1.7	1.6	1.5	1.5

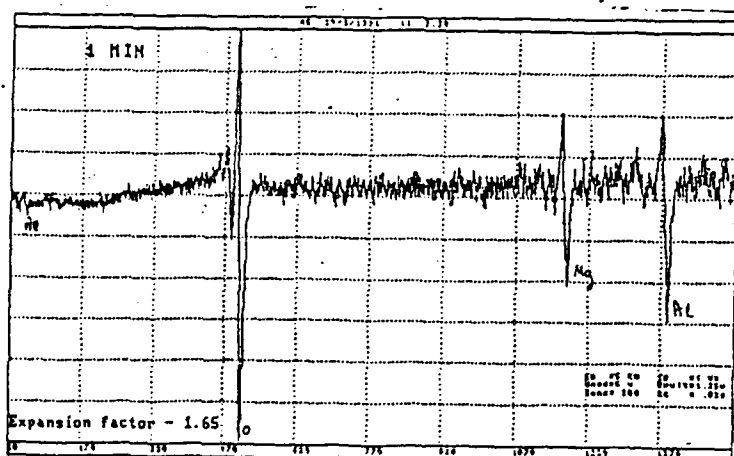




A



B



C

Fig. 12: Auger surface analysis of untreated Al (a), 200P (b), and 2000 P (c) laser treated Al samples.

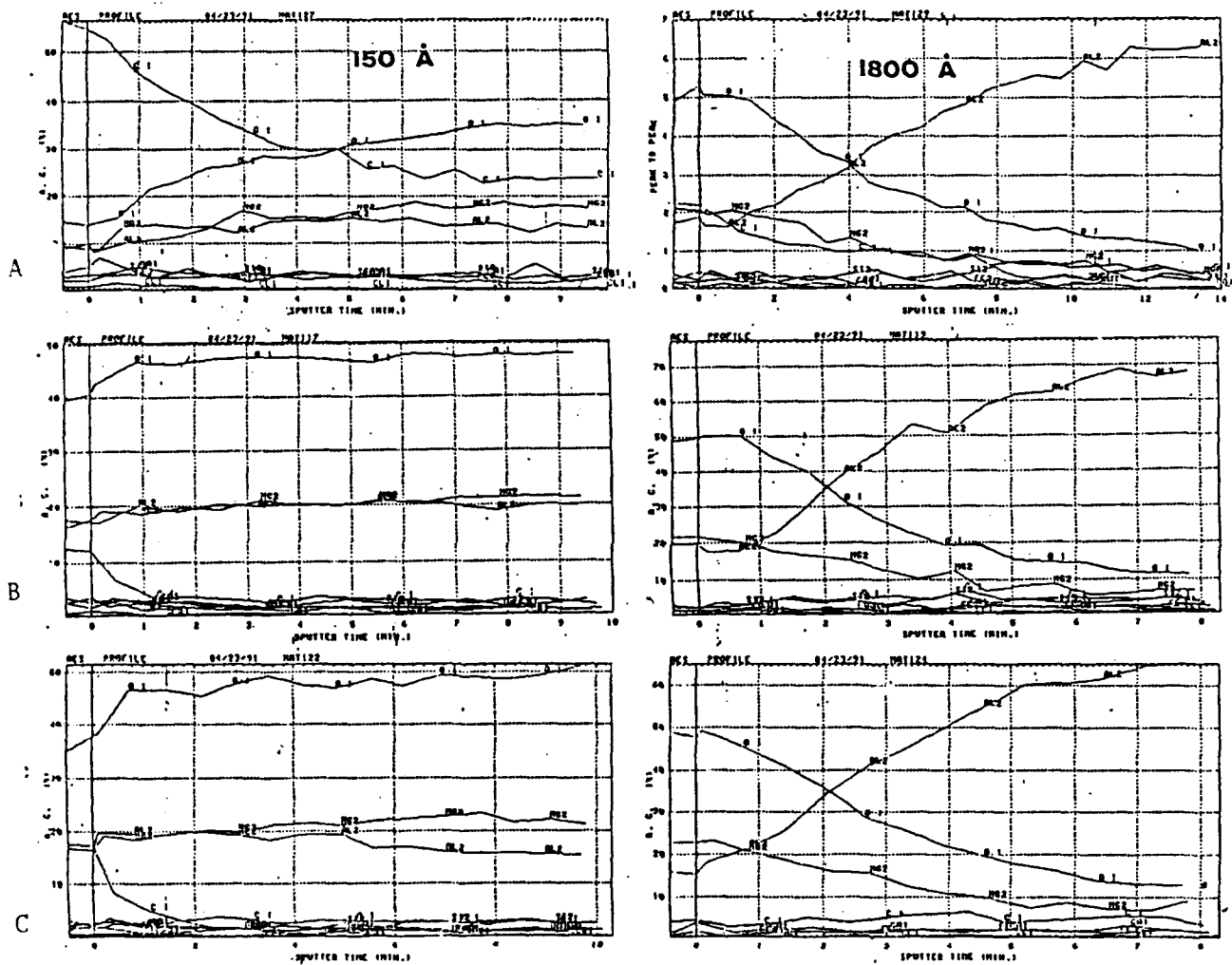


Fig. 13: Auger depth analysis of untreated Al (a), 200P (b), and 2000 P (c) laser treated Al.

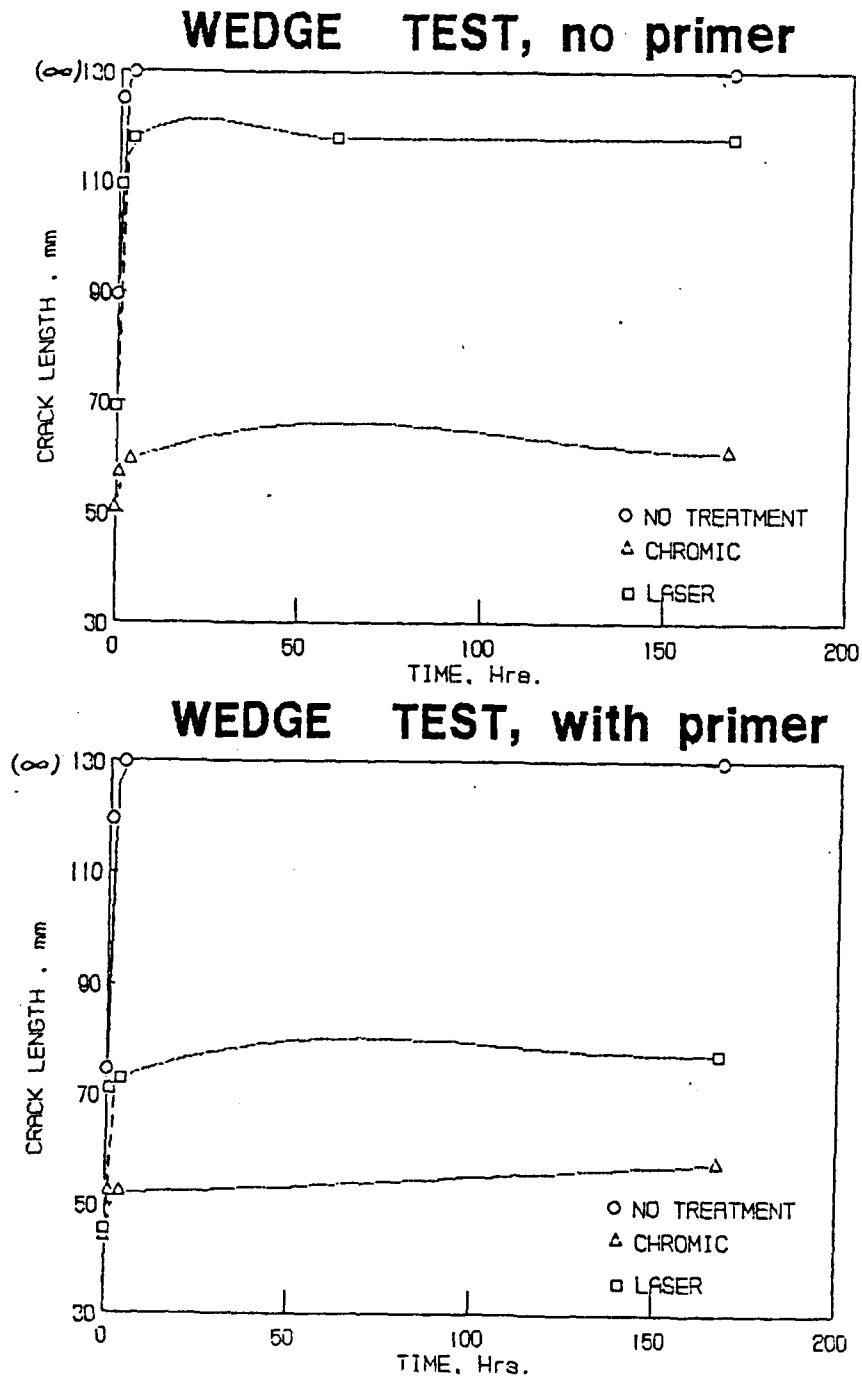
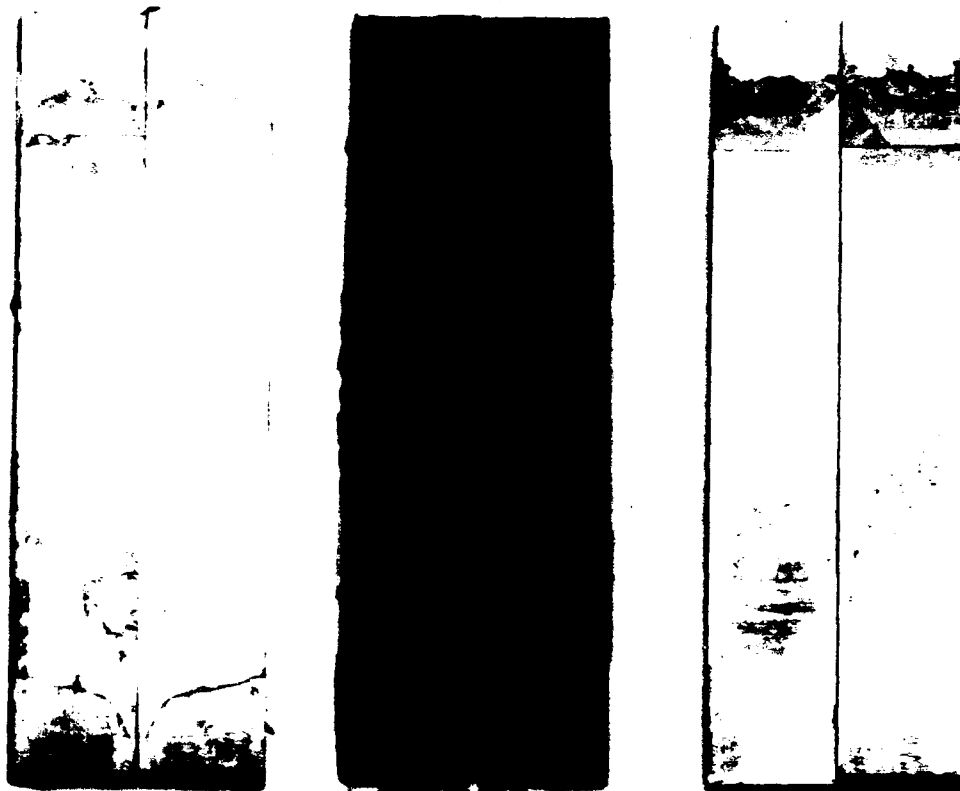


Fig. 14: Summary of results of wedge tests. Laser treatment: 2000 pulses at $0.185 \text{ J/P} \cdot \text{cm}^2$.

WEDGE TEST WITHOUT PRIMER



28
IN

NO TREATMENT CHROMIC ANODIZATION LASER TREATMENT
(NON - SEALED)

WEDGE TEST WITH PRIMER



NO TREATMENT CHROMIC ANODIZATION LASER TREATMENT
(NON - SEALED)

Fig 14b: General view of the open wedge samples after enviromental exposure.

It can be seen that although the adhesion shear strength of the bare treated Al is higher than that of the primed one, its durability is lower. Durability of laser treated and primed Al adherent is close to that of anodized non-sealed aluminum and the mode of failure is the same.

4. CONCLUSIONS

Excimer ArF laser, which interacts chemically and physically, provides an effective preadhesion treatment to 2024 Al alloy. The effect of laser treatment depends upon time of exposure and laser energy. High laser energy treatment results in high adhesion shear strength which, at optimal conditions ($0.185 \text{ J/P}\cdot\text{cm}^2$), exceeded even that of the chromic anodized unsealed preadhesion treatment of Al alloys.

Applying a primer on the laser treated adherend results in the same effect but with slightly suppressed shear strength but still exceeding the chromic anodized treatment.

Laser treatment of primed adherents resulted only in a slight improvement of shear strength which was below the values obtained for chromic anodization.

The enhanced mechanical properties were supported by visual inspections and SEM micrographs indicating a change of failure mode from adhesive (nontreated) to mostly cohesive (laser treated). At higher number of pulses the changes of Al surface morphology were correlated with the enhanced adhesion strength.

FTIR studies revealed chemical changes on the surface including growth of an oxidized layer at optimal laser conditions ($0.185 \text{ J/P}\cdot\text{cm}^2$) and hydration of the oxide layer at high laser energies ($0.73 \text{ J/P}\cdot\text{cm}^2$). Primer ablation was obvious at high pulse number which explains the decreased shear strength of these specimens.

Durability studies of the laser pretreated joints in hot-humid environments proved that the laser treatment is durable to hygrothermal environment when primed before adhesion close to the durability attained with chromic anodization.

It can be concluded that ArF laser treatment has been demonstrated to be an effective, clean, and simple method for surface pretreatment of aluminum (as well as polymeric adherends) compared to conventional etching and abrading methods.

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